Baseline

Accumulation and distribution of trace metals within soils and the austral cordgrass *Spartina densiflora* in a Patagonian salt marsh

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ABSTRACT

Concentrations of Cd, Cu, Fe, Pb, and Zn were determined in soils and in below- and above-ground structures of *Spartina densiflora* in a Patagonian salt marsh (San Antonio, Río Negro, Argentina). Also, the relationship between trace metal concentrations in soils and plants was investigated to improve our knowledge regarding the ability of this plant species to take up and accumulate trace metals from the soil. Our results indicate that, within the studied salt marsh, soil trace metal concentrations follow a decreasing concentration gradient toward the sea. They show moderate pollution and a potentially negative biological effect in one site of the salt marsh. While below-ground structures reflect the soil metal concentration pattern, this is not so evident in above-ground concentrations. Also, *S. densiflora* is able to absorb a limited amount of metals present in the soil, the soil bioaccumulation factor being lower in sites where soil metal concentration is higher.

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Studies concerning the impact of different pollutants such as trace metals, oil, pesticides, and fertilizers on coastal and estuarine environments have increased during the last decades. The presence of trace metals in the soil has mainly lithogenic origin, which is sometimes increased by anthropogenic factors (e.g., agricultural practices and industrial activities). Also, the contamination could be localized and derived from a predominant single source, such as a metal smelter, having a marked effect on soils, plants and even in the health of a local population (Alloway, 2010). Environmental pollution due to chemical toxic substances determines a risk to the health of ecosystems as well as to human life.

The presence of trace metals within the San Antonio Bay (Río Negro Province, Argentina) is well documented (Gil et al., 1996, 1999; Esteves et al., 2004; Vázquez et al., 2007). During the 60s and 80s a mine which extracted zinc, lead, silver and vanadium operated near the San Antonio Oeste City. At the same time, an electrochemical plant was established close to the city for the processing of trace metal ores excavated from the mine. As a consequence, at the upland border of San Antonio Bay there is an open-air dump where the wastes of the processing activities have been piled for over three decades. This residual material from mining activities is subjected to infiltration and leaching when it rains. While at present there are only remnants, previous studies show the presence of trace metals in the sediment and marine invertebrates of the Bay, with a marked concentration gradient in the positive direction west–east (Gil et al., 1999; Esteves et al., 2004; Vázquez et al., 2007).

The San Antonio Bay is surrounded by an extensive salt marsh. These natural features are highly productive environments, and have a very important ecological role due to the fact that they are reproductive and feeding sites for a lot of species, both marine and terrestrial (Mitsch and Gosselink, 2000). These environments can absorb trace metals from the surrounding ecosystems, which may be immobilized and stored in the soil as biologically unusable forms (Hung and Chmura, 2007; Botté et al., 2010) or be absorbed by plants (Hempel et al., 2008; Caçador et al., 2009; Redondo-Gómez et al., 2009; Duarte et al., 2010; Almeida et al., 2011). When trace metals enter salt marshes, they can be absorbed by plants, being either retained in their underground structures or translocated to their aerial structures; depending on the plant species, the physicochemical soil features, and the metal (Weis and Weis, 2004). By absorbing metals plants mobilize them from the soil to the trophic web, either to be consumed directly by herbivores, or through plant debris that are incorporated in the basal level of the food chain, where bioaccumulation (or even biomagnification) may occur through higher trophic levels (Wang, 2002; Barwick and Maher, 2003; Croteau et al., 2005; Rainbow et al., 2006; Beltrame et al., 2010; Simonetti et al., 2012). In this sense, trace metal pollution does not only have a negative effect on soils, which has an impact on plants, but also affects animals, representing a serious risk to the ecosystem.

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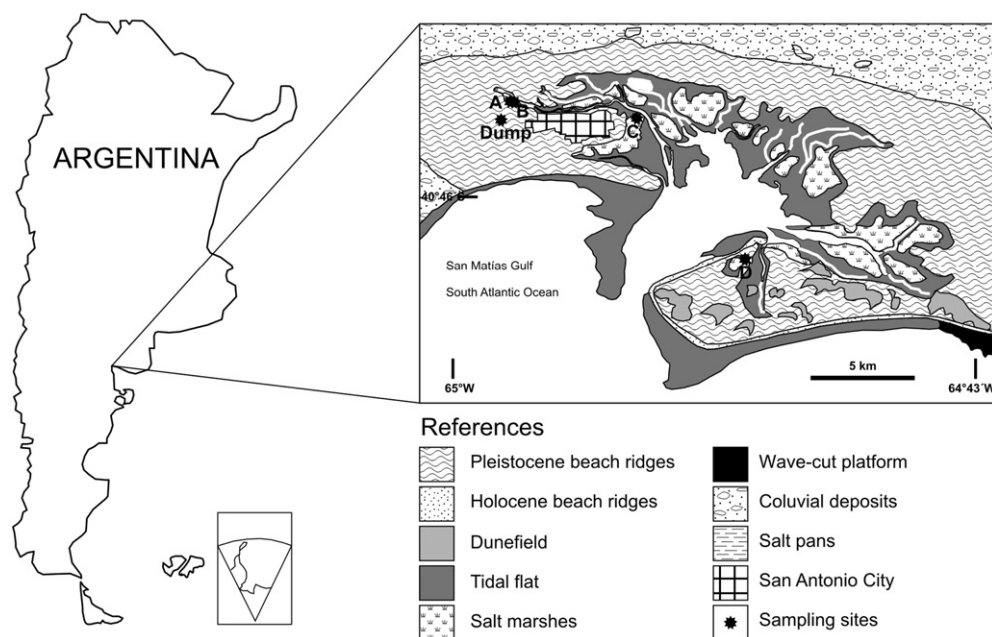E-mail address: idaszkin@cenpat-conicet.gob.ar (Y.L. Idaszkin).

Fig. 1. Main geomorphological units and location of the sampling sites in the San Antonio salt marsh in Argentina.

The surrounding salt marsh is inhabited by perennial halophytics *Spartina alterniflora* and *Spartina densiflora* (Poaceae). The austral cord-grass *S. densiflora* is a common perennial species of middle and high marsh levels in Patagonian salt marshes (Isacch et al., 2006; Bortolus et al., 2009). *S. densiflora* is a C_4 species native of South American coastal marshes, and is invading successfully salt marshes of North America, Spain, Portugal and North Africa (Bortolus, 2006). It is a widespread species, whose distribution range includes very different climate conditions and environmental scenarios (Bortolus, 2006; Idaszkin et al., 2014a), including polluted salt marshes, where they grow in soils with high concentrations of heavy metals (Redondo-Gómez, 2013; Curado et al., 2014). Although there are studies in the San Antonio Bay (Gil et al., 1999; Esteves et al., 2004; Vázquez et al., 2007), to date there is no research evaluating the levels of trace metals in the salt marsh. The main purpose of this study was to determine the concentrations of Cd, Cu, Fe, Pb, and Zn in soils and *S. densiflora* in a Patagonian salt marsh (San Antonio, Río Negro, Argentina). Also, we investigated the relationship between trace metal concentrations in soils and in plants to improve our knowledge regarding the ability of these plant species to take up and accumulate trace metals from the soil.

The present study was conducted within the salt marsh surrounding the San Antonio Bay (hereafter called "San Antonio salt marsh"; 40°44′S, 54°68′W), a Natural Protected Area (Río Negro, Argentina; Fig. 1). This salt marsh is a strictly marine system with a semidiurnal macro-tidal regime (tidal amplitude: ~9 m), and is crossed by several tidal channels. Specifically, three sampling sites were selected within the salt marsh adjacent to the main tidal channel (Fig. 1). The site "A" is nearest to the head of this channel, and is the closest to the largest open-air dump, that due to the topography is a zone largely influenced by the mine superficial run-off erosion. The second site "B" is located nearest the above site and the site "C" is in the outer zone of the channel. A fourth site "D" was placed also out of the Bay. All sampling sites were within the high salt marsh level dominated by *S. densiflora* and *Sarcocornia perennis*, accompanied by *Limonium brasiliense* and *Atriplex* spp. in low proportions (Isacch et al., 2006; Bortolus et al., 2009).

At each site, five core samples were collected in spring 2013 from *S. densiflora* (hereafter called "*Spartina*") stands, all with a distance of 1 m from each other obtained at low tide. Each core sample (15-cm-diameter and 15-cm-depth) consisted of plants (below- and above-ground structures) and surrounded soils of below-ground plant tissues.

Table 1
Soil parameters in the San Antonio salt marsh (mean ± S.E.).

Soil parameters	Site A		Site B		Site C		Site D	
	Non-vegetated soil	*Spartina* soil	Non-vegetated soil	*Spartina* soil	Non-vegetated soil	*Spartina* soil	Non-vegetated soil	Spartina soil
EC (mm hos cm^{-1})	(7.68 ± 0.76)	(9.2 ± 1.15)	(7.27 ± 0.37)	(6.57 ± 0.45)	(3.97 ± 0.1)	(3.75 ± 0.06)	(3.55 ± 0.52)	(3.41 ± 0.31)
Eh (mV)	(142.8 ± 7.36)	(139.6 ± 7)	(143.75 ± 15.1)	(163.2 ± 11.59)	(167 ± 4.01)	(147.2 ± 10.64)	(162.75 ± 5.92)	(189.6 ± 13.87)
pH	(7.66 ± 0.05)	(7.61 ± 0.02)	(7.51 ± 0.01)	(7.68 ± 0.05)	(7.65 ± 0.04)	(7.54 ± 0.05)	(7.74 ± 0.06)	(7.63 ± 0.05)
OM (%)	(5.84 ± 0.41)	(6.46 ± 0.26)	(4.49 ± 0.34)	(5.69 ± 0.64)	(3.08 ± 0.09)	(2.93 ± 0.13)	(2.45 ± 0.26)	(2.55 ± 0.29)
Clay (%)	(18.86 ± 4.09)	(22.63 ± 3.81)	(20.04 ± 2.38)	(14.97 ± 1.03)	(3.85 ± 0.59)	(3.87 ± 0.33)	(4.91 ± 0.89)	(6.1 ± 0.48)
Silt (%)	(52.04 ± 6.49)	(55.57 ± 3.29)	(50.51 ± 4.13)	(52.54 ± 5.48)	(27.41 ± 0.66)	(30.26 ± 1.2)	(26.56 ± 1.73)	(23.75 ± 3.33)
Fine silt (%)	(25.04 ± 4.32)	(27.22 ± 2.64)	(26.4 ± 4.32)	(30.32 ± 3.97)	(13.58 ± 0.99)	(14.33 ± 1.72)	(10.12 ± 0.71)	(9.82 ± 2.41)
Coarse silt (%)	(27 ± 2.35)	(28.34 ± 1.55)	(24.11 ± 0.82)	(22.21 ± 1.76)	(13.83 ± 0.51)	(15.93 ± 0.99)	(16.44 ± 1.45)	(13.93 ± 1.62)
Fine fraction (%)	(70.9 ± 5.42)	(78.2 ± 2.07)	(70.55 ± 6.18)	(67.5 ± 6.28)	(31.26 ± 1)	(34.13 ± 1.02)	(31.48 ± 1.28)	(29.85 ± 3.68)
Sand (%)	(29.09 ± 5.42)	(21.79 ± 2.07)	(29.45 ± 6.18)	(32.5 ± 6.28)	(68.74 ± 1)	(65.87 ± 1.02)	(68.52 ± 1.28)	(70.15 ± 3.68)
Cu (µg g^{-1})	(38.72 ± 3.99)	(38.86 ± 1.76)	(10.8 ± 0.86)	(13.32 ± 2)	(4.98 ± 0.21)	(5.62 ± 0.14)	(5.13 ± 1.23)	(5.92 ± 1.01)
Fe (µg g^{-1})	(14,234 ± 735)	(14,536 ± 180)	(12,055 ± 836)	(12,464 ± 880)	(12,991 ± 569)	(13,994 ± 291)	(13,701 ± 1627)	(14,552 ± 1645)
Pb (µg g^{-1})	(63.9 ± 7.24)	(66.22 ± 3.53)	(13.75 ± 1.85)	(14.52 ± 2.53)	(7.66 ± 0.35)	(8.22 ± 0.22)	(4.3 ± 1.25)	(4.94 ± 0.79)
Zn (µg g^{-1})	(221.6 ± 24.82)	(222.4 ± 4.65)	(47.5 ± 5.85)	(62.2 ± 10.73)	(17.2 ± 0.74)	(19.56 ± 0.48)	(17.85 ± 1.08)	(19.68 ± 1.04)

Five samples of non-vegetated soil in each site were also collected. The redox potential (Eh) and pH of the soil in the below-ground tissues zone (0–10 cm) and of non-vegetated soil were determined in the field using a portable pH/Eh (ORP) meter and electrode system Termo/pH meter Altronix TPA-IV. Samples were stored in polyethylene bags, transported to the laboratory and frozen to −20 °C until analyzed.

The surrounded soils of below-ground plant structures were collected. All soil samples were dried at 80 °C until constant weight and sieved through a 2 mm mesh to remove large stones and dead plant material. Electrical conductivity (EC) was measured with a conductivity meter in a 1:5 soil water extract. Percentages of sand, silt, and clay were estimated using the Pipette method (Day, 1965). Organic matter (OM) was determined by the loss on ignition method (4 h at 450 °C) (Davies, 1974).

Regarding plant samples, they were carefully washed with tri-distilled water and separated into below-ground tissues (roots and rhizomes) and above-ground tissues (stems and leaves). All samples were dried at 80 °C until a constant weight was reached and pulverized in a mill until the powder was fine enough to pass through a 1 mm sieve.

For the analysis of metals, 1 g of dried and sieved soil or 0.5 g of dried plant material was digested in 2 ml of HNO_3 (Merck) ultrapure using microwave oven MARS-5, CEM Corporation, USA (2011) and was then diluted to a final volume of 15 ml with nitric acid (EPA, 2000). Cadmium (Cd), copper (Cu), iron (Fe), lead (Pb), and zinc (Zn), in both matrixes were then measured by inductively coupled plasma (ICP-AES) spectroscopy (Shimadzu 9000). In all cases, the average uncertainty of metal ion determination was <2%. All extractions were carried out in duplicate and blanks were processed as the samples. Results are reported on a dry weight.

Reagents of analytical grade were used for the blanks and for calibration curves. Quality assurance of soils and plants was done through analysis of standard reference freshwater sediment CNS392-050 and BCR-060 aquatic plant (*Lagarosiphon major*), respectively. The recovery in soil sample varied between 87% for Zn to 98% for Fe, while in plant tissues it was >96% for all metals.

Concerning data analysis, confidence intervals were generated for the average value of each of the measurements made by site, soil type, and plant structure. The intervals were generated by taking random samples with replacement n = sample size (e. g., faith to site A, above-ground) and calculating the average value of the sample obtained. This step was repeated 3000 times, and a confidence interval was generated based on the resulting 3000 estimations of the average values. The differences between sites, soil types or plant structures were evaluated by comparing the confident intervals at $\alpha = 0.05$ level with Student's t-test. Also, Pearson coefficients (r) were calculated to evaluate correlations between different soil parameters.

There was an overall increase in soil trace metal concentrations measured from site A to sites C and D, independently from the plants' presence (Table 1, Fig. 2). This may reflect the role of the open-air dump as main source of trace metals to the salt marsh, nearest to the head of this channel, and from there these metals are dispersed to the mouth of the Bay by the action of rainfall or tidal cycles due to the topography of the marsh. Moreover, as we expected, all the metal concentrations that we found followed the same gradient west–east reported for sediments of the tidal channel for the Bay, outside the salt marsh (Gil et al., 1999; Esteves et al., 2004; Vázquez et al., 2007). In all cases, the highest value was measured for Fe, followed by Zn, Pb, and Cu. Cadmium was always <0.1 μg g^{-1}. When we compared trace metal concentrations
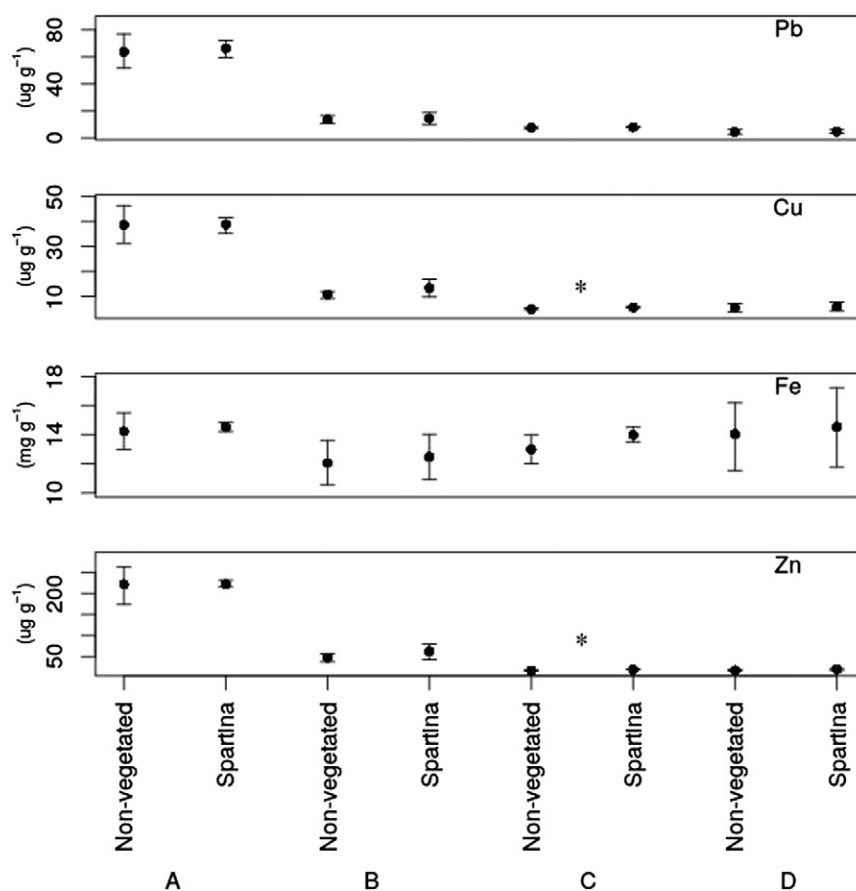

Fig. 2. Confident intervals of trace metals in two soil types of the sample sites in the San Antonio salt marsh (site locations are shown in Fig. 1). Points and bars represent respectively the mean value and the error (95% confidence interval). * indicates significant differences (p < 0.05).

between soil types within each site, we found scarce significant differences. In site C Cu and Zn in soil associated with *Spartina* were higher than in non-vegetated soil (Cu: p = 0.023, t = 2.51; Zn: p = 0.013, t = 2.67; Fig. 2). In a general sense, in the San Antonio salt marsh the concentration of the studied metals remains unaffected by the plant presence (Fig. 2). In this regard, there are studies that support our findings and others that present opposing results. While several studies have recorded higher metal concentration in soils associated to *Spartina maritima* roots than in soils without roots (Caçador et al., 1996; Reboreda and Caçador, 2007; Reboreda et al., 2008). Cambrollé et al. (2008, 2011) found this pattern in the Odiel marsh (SW Spain), but not in the Tinto marsh (SW Spain).

Regarding soil parameters in each site, only the pH showed significant differences between soil types in all sites (Table 1; Fig. 3). However, other variables except the Eh and clay showed only significant differences within the site C (Table 1; Fig. 3). In addition, all soil parameters showed significant differences between sites in the San Antonio salt marsh (Table 1; Fig. 3). The OM content as the EC were the highest in soils of site A followed by sites B, C, and D. Although the pH was statistically different between soil types and sites, it was always slightly basic.

Similarly, being statistically different, the Eh was oxidized in all cases. On the other hand, the textures in sites A and B were silty loam, the fine silt being the major fraction followed by coarse silt and clay, while the textures in sites C and D were sandy loam. Moreover, trace metal concentrations in soils did not show a clear correlation pattern with the measured soil parameters within each site (Fig. 4). Every metal correlated with the OM in site B and with the EC in site D. Instead, in all sites, they all correlated with at least one of the textural variables. These significant correlations were positive except in those including clay and sand. However, when we polled the sites, significant positive correlations were observed among Cu, Pb and Zn and the measured soil parameters, except the pH (Table 2, Fig. 4). Both the OM and the fine fraction (clay + silt) were mentioned as key factors that favor the concentration of trace metals in salt marsh soils (Fitzgerald et al., 2003). All the relations among metals resulted positive in sites C and D (Fig. 4). However, only Pb–Cu, Pb–Zn, Pb–Fe and Zn–Cu showed significant positive correlations in site A, and the same was observed between Pb–Cu, Pb–Zn, Cu–Fe and Zn–Cu in site B (Fig. 4). These patterns suggest that the studied metals have a similar biogeochemical behavior in addition to probable common sources.
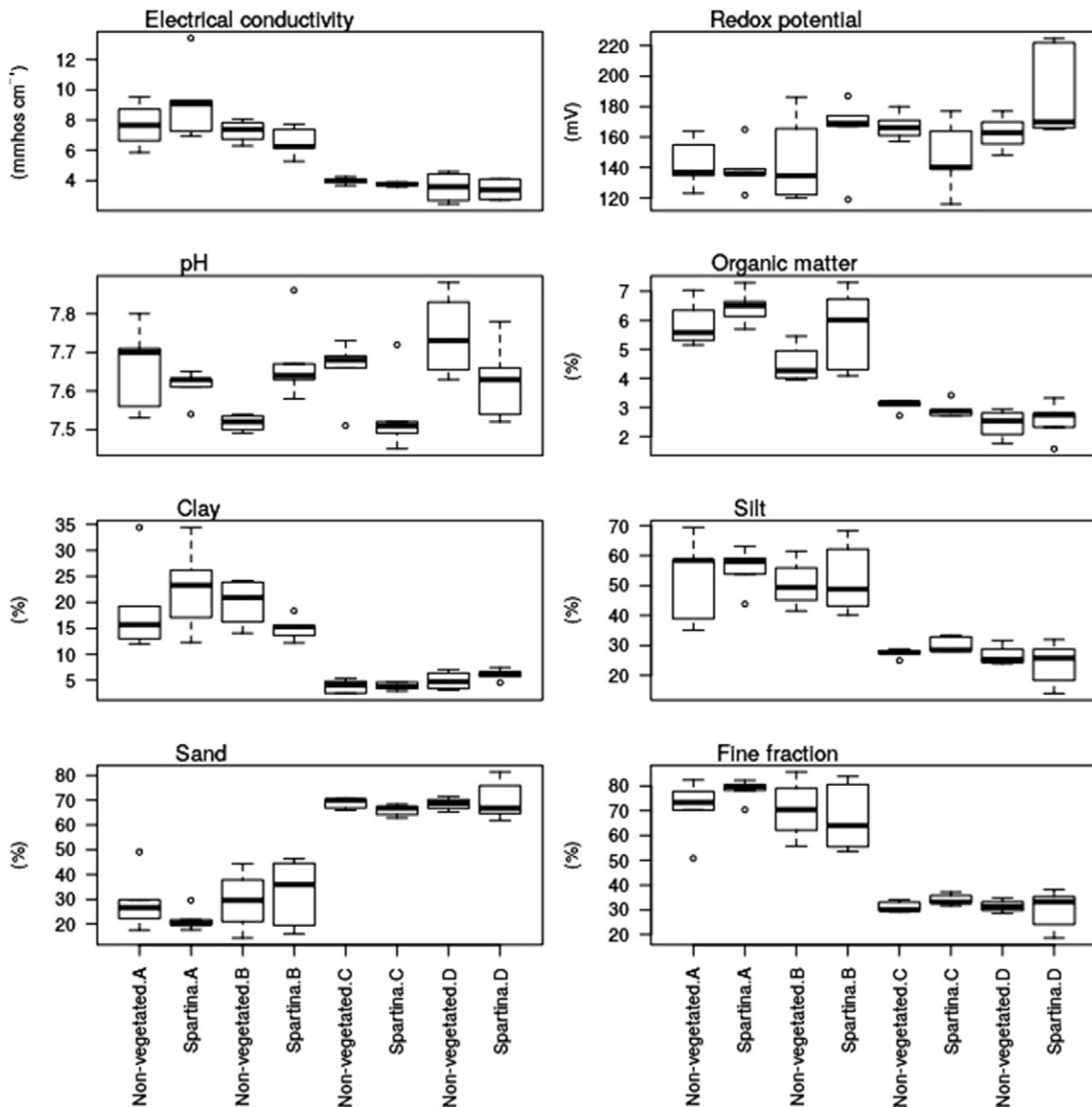

Fig. 3. Soil parameters in two soil types of the sample sites in the San Antonio salt marsh (site locations are shown in Fig. 1). Horizontal lines in boxes represent median values of metal concentration. The lower and upper hinges represent 25 and 75% percentiles respectively. * indicates significant differences (p < 0.05) between soil types.
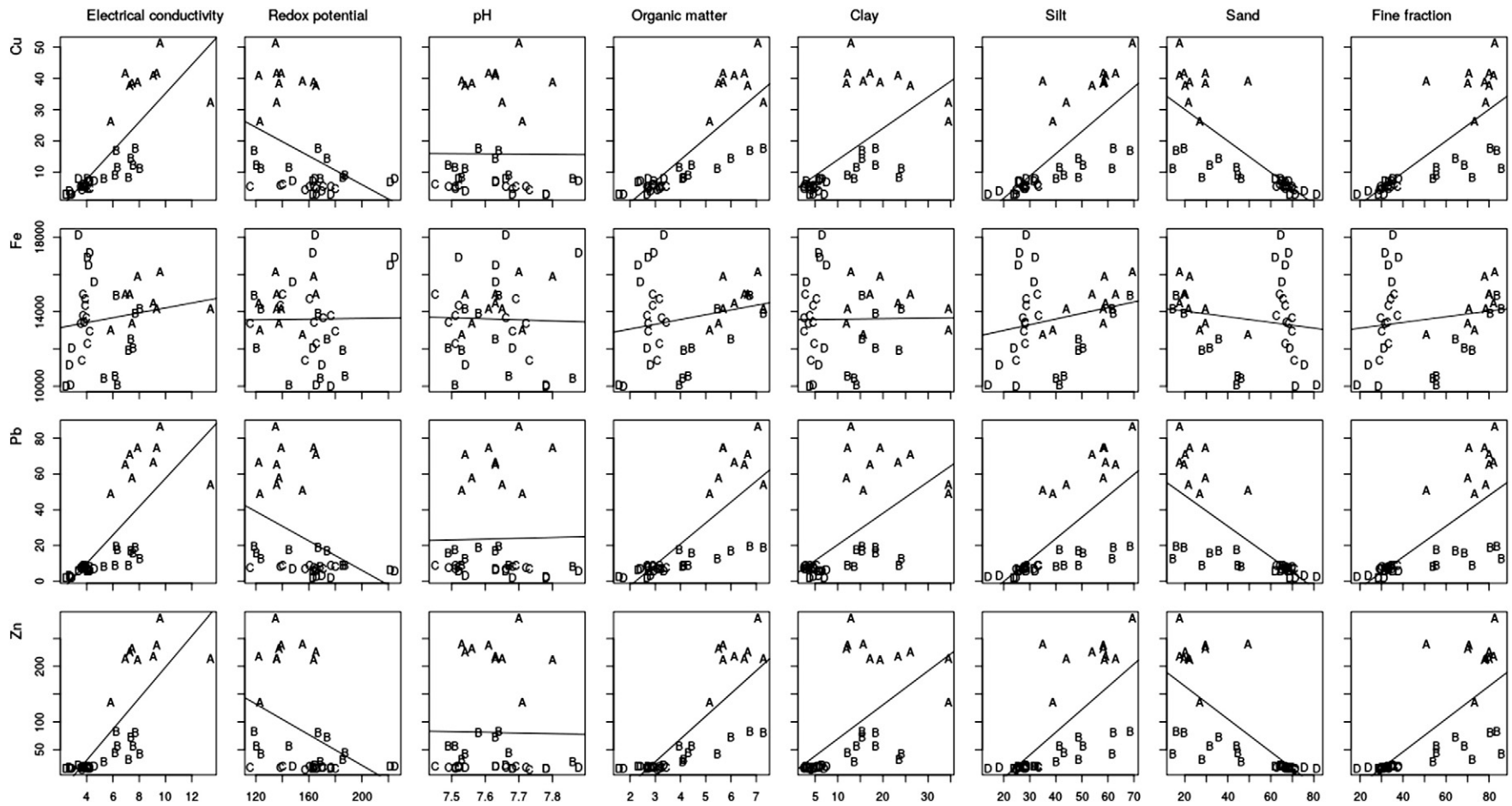
Fig. 4. Pseudototal concentration of four trace metals against eight soil parameters in the San Antonio salt marsh. Capital letters indicate each sample site (site locations are shown in Fig. 1). Lines in figures show the expected values based on a lineal model fitted with all sites in a single group for each variable and trace metal.

Table 2
Pearson correlation coefficients (r) between soil parameters and pseudototal trace metal concentrations in soils.

|	Cu	Fe	Pb	Zn
EC (mm hos cm^{-1})	0.78[*]	0.15	0.74[*]	0.79[*]
Eh (mV)	−0.4[*]	0.01	−0.4[*]	−0.39[*]
pH	−0.01	−0.03	0.02	−0.01
OM (%)	0.81[*]	0.21	0.76[*]	0.81[*]
Clay (%)	0.6[*]	0.01	0.6[*]	0.61[*]
Fine silt (%)	0.61[*]	0.22	0.56[*]	0.57[*]
Coarse silt (%)	0.83[*]	0.2	0.81[*]	0.8[*]
Silt (%)	0.74[*]	0.23	0.7[*]	0.7[*]
Sand (%)	−0.76[*]	−0.16	−0.73[*]	−0.73[*]
Fine fraction (%)	0.76[*]	0.16	0.73[*]	0.73[*]

[*] $p < 0.05$.

To evaluate the extent of trace metal contamination in the studied salt marsh and the probable risk to the organisms, Canadian Sediment Quality Guidelines (Canadian Council of Ministers of the Environment, CCME, 2002) have been used because sediment quality guidelines do not exist in Argentina and because these guidelines were established using a similar extraction method (mild digestion) to that applied in the present study (nitric acid). They provide two reference values: the threshold effect level (TEL) represents the trace metal concentration below which adverse biological effects are expected to occur rarely, and the probable effect level (PEL) represents the trace metal concentration below which adverse biological effects are expected to occur frequently (Wang et al., 2014). In this regard, concentrations lower than the TEL indicate minor pollution, concentrations higher than the PEL indicate high pollution level, while trace metal concentration lying between those values indicates moderate pollution. In the San Antonio salt marsh, within site A, soil concentrations of Cu, Zn and Pb were between the TEL and the PEL, denoting moderate pollution and that could result in some degree of negative biological effect (TEL$_{Cu}$ = 18.7, TEL$_{Pb}$ = 30.2, and TEL$_{Zn}$ = 124 µg g^{-1} dry wt; PEL$_{Cu}$ = 108, PEL$_{Pb}$ = 112, and PEL$_{Zn}$ = 271 µg g^{-1} dry wt). At the same time, on the other sites soil concentrations of these metals are below the TEL suggesting negligible pollution. In general terms, it can be suggested that trace metals have a low ecological risk in the studied salt marsh.

Every trace metal detected in the soils was found at concentrations high enough to be quantifiable in all *Spartina* plant samples (Fig. 5a, b). However, these metals did not reach the potential phytotoxic levels for the leaves in the plants of the San Antonio salt marsh (20–30 µg Cu g^{-1}, 100–300 µg Zn g^{-1}, 30–300 µg Pb g^{-1} and >1000 µg Fe g^{-1}; according to Kabata-Pendias and Pendias, 2001; Broadley, 2012; Mateos-Naranjo et al., 2013).

In all sites, *Spartina* concentrated statistically more Cu, Fe, and Zn in below-ground structures than in above-ground structures (Fig. 5a, b). Furthermore, it concentrated significantly more Pb in the below-ground than in above-ground structures only in sites A and B (Fig. 5a).
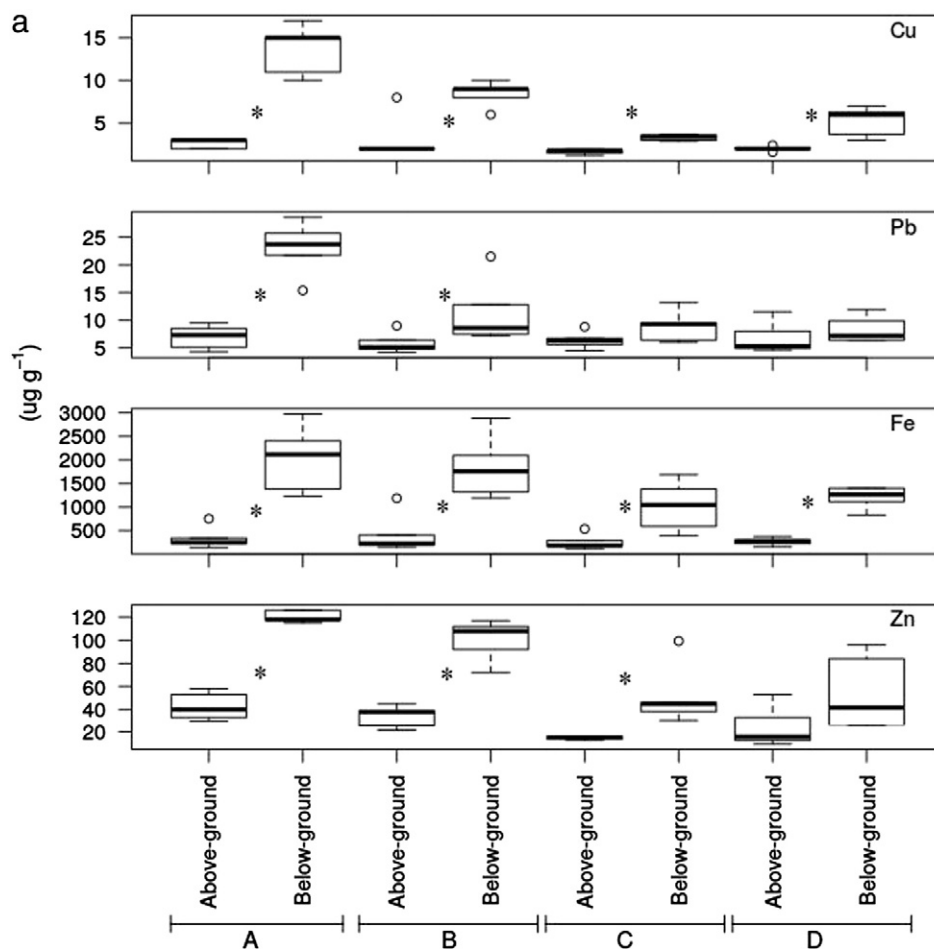
Fig. 5. Trace metal concentration in below- and above-ground structures of *Spartina densiflora* in the San Antonio salt marsh. Horizontal lines in boxes represent median values of metal concentration. Lower and upper hinges represent 25 and 75% percentiles respectively. Upper panel (a) shows comparatively metal concentrations between structures (above- and below-ground) for the four sampled sites (site locations are shown in Fig. 1). * indicates significant differences (p < 0.05). Lower panel (b) shows the metal concentration between sites for structures above- and below-ground. Letters indicate the sites that were significantly different (p < 0.05). Comparisons were done using pairwise resampling analysis based on a Student's t-test.
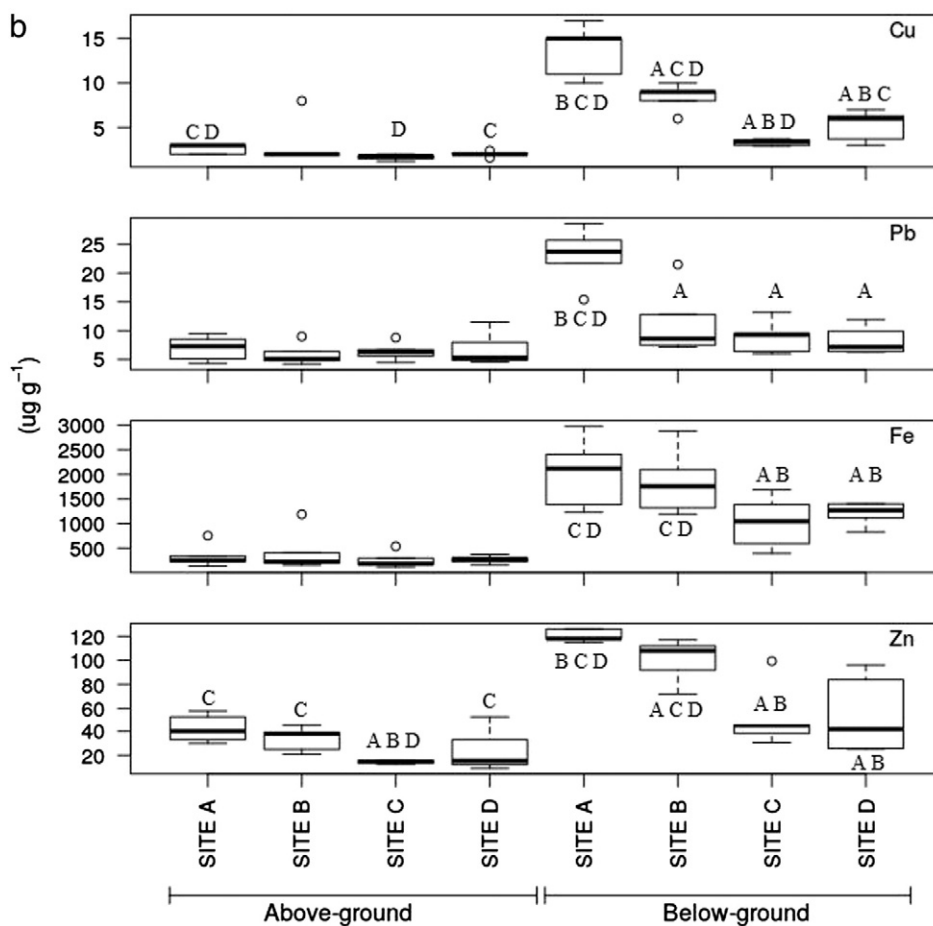
Fig. 5 (*continued*).

Regarding statistic differences in trace metal concentrations in above-ground, *Spartina* concentrated significantly less Zn in above-ground structures in site C; significantly more Cu in site A than in sites C and D, while Fe and Pb in above-ground structures did not show significant differences among sites (Fig. 5b). In relation to below-ground structures, it concentrated significantly more Pb in plants from site A; more Fe and Zn in plants from sites A, and B; and more Cu in site A, followed by plants from sites B, D and then C (Fig. 5b). While below-ground structures reflected the soil metal concentration pattern, this was not so evident in above-ground concentrations. These results are consistent with findings of previous studies, which found that different *Spartina* species, including *S. densiflora*, minimize the translocation of trace metals to the photosynthetic tissues (Reboreda et al., 2008; Cambrollé et al., 2008, 2011; Duarte et al., 2010; Curado et al., 2014; Idaszkin et al., 2014b). It has been showed that when potentially toxic elements are taken up, plants may avoid toxicity in the above-ground parts by restricting the translocation from below-ground structures, effective re-translocation of the element from the above-ground parts back to the below-ground where they may be accumulated or even excreted (Weis and Weis, 2004; Redondo-Gómez, 2013). Also, some halophytes have salt glands in their leaves to the excretion of excessive concentrations of toxic elements in the above-ground structures (Burke et al., 2000; Weis and Weis, 2004; Redondo-Gómez et al., 2011). We do not know the mechanism or mechanisms that act in these plants, which could be evaluated in the future. All the same, it is well established that the degree of uptake and the distribution of metals within plant structures differ upon the metal ion uptake routes, the metal speciation and bioavailability and the plant species (Williams et al., 1994; Redondo-Gómez, 2013).

To estimate the capability of *Spartina* to take up and accumulate trace metals present in the soil in underground tissues, soil-bioaccumulation factors (SBAF: [trace metal in below-ground structures] / [trace metal in soils]; Mason, 2013) were calculated. *Spartina* plants from site A had significantly lower Cu–, Pb–, and Zn–SBAF than plants from the other sites (Fig. 6). Conversely, Fe–SBAF was higher for plants from sites A and B (Fig. 6). Also, results suggest that *Spartina* is able to accumulate in below-ground structures (SBAF > 1) Cu, Pb, and Zn in some sites of the San Antonio salt marsh (site D for Cu, sites C and D for Pb, and sites B, C, and D for Zn). In this regard, it appears that *Spartina* is able to absorb a limited amount of metals present in the soil, provided that the SBAF was lower in sites where soil metal and below-ground concentrations are higher. These results may be related to differences in the bioavailability of the trace metals, considering that edaphic conditions are different between sites C and D and sites A and B (Fig. 3). Possibly, physico-chemical conditions in the root zone may be limiting the incorporation of trace metals into the plants due to the fact that they strongly affect their geochemical partitioning. In this respect, most of the trace metals could be in low mobility forms (e.g., adsorbed on particle surfaces, bound to the mineral matrix of the sediment, carbonate, organic matter, sulfide or in Fe/Mn oxide surface coatings; Kabata-Pendias and Pendias, 2001). Therefore these trace metal forms may not be readily available to be absorbed by plants.

Our results show that the San Antonio salt marsh has an important role in capturing metals that have been washed from the source inland, reducing their access to the bay and, in turn, to the ocean. The low transfer to the aerial structures is also an important point, because it promotes their detention and transfer to different trophic levels.
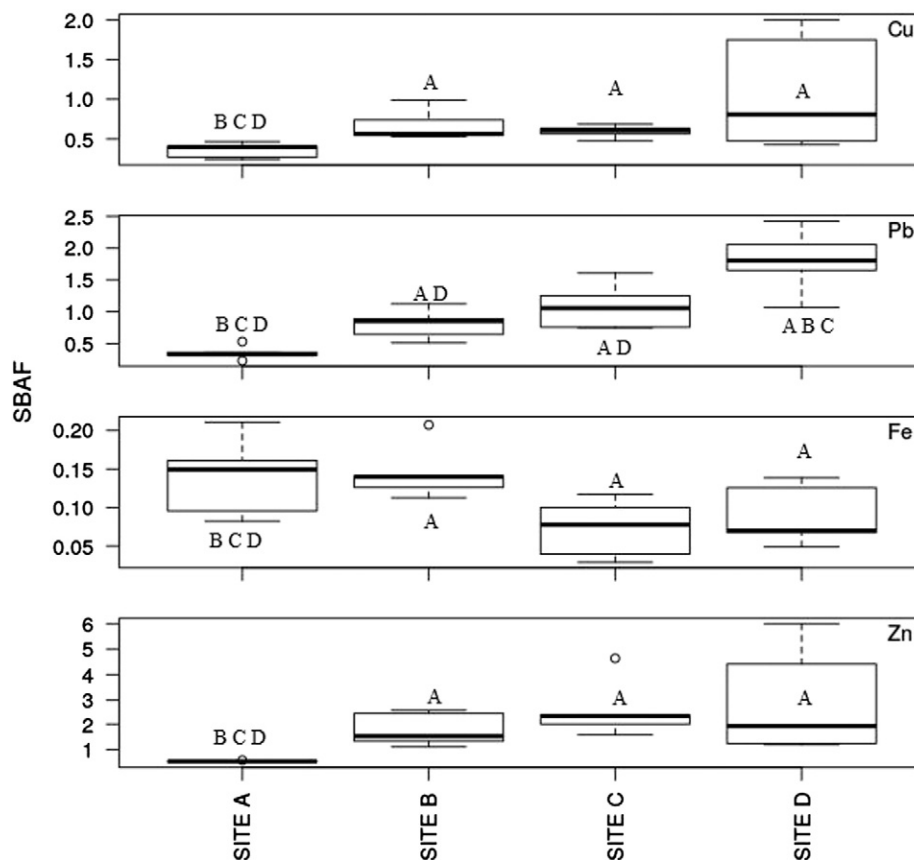
Fig. 6. Soil bioaccumulation factor (SBAF) in below-ground structures of *Spartina densiflora* in the sample sites in the San Antonio salt marsh (site locations are shown in Fig. 1). Horizontal lines in boxes represent median values of metal concentration. The lower and upper hinges represent 25 and 75% percentiles respectively. Letters indicate the sites that were significantly different (p < 0.05), evaluated with pairwise comparison based on resampling analysis with Student's t-test.

Acknowledgments

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